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## HREM STUDIES OF COHERENT AND INCOHERENT INTERFACES IN $ZrO_2$ -CONTAINING CERAMICS: A PRELIMINARY ACCOUNT

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HREM has been applied to the study of interfaces in various  $ZrO_2$ -containing ceramics. In dispersion-toughened ceramics, such as  $ZrO_2$ -toughened  $Al_2O_3$ , fine  $ZrO_2$  particles can be either *intra-* or *inter-* granular. *Intragranular*  $ZrO_2$  particles form *incoherent* interfaces with their  $Al_2O_3$  hosts, and such interfaces have been imaged by HREM. The interfaces between *inter-* granular  $ZrO_2$  particles and  $Al_2O_3$  grains are generally covered with a glassy phase, 1-3 nm in thickness, and evidence for this phase is also present in HREM images. If the  $ZrO_2$  transforms from tetragonal to monoclinic symmetry during cooling from the fabrication temperature, it is generally twinned, and the *coherent* twin boundaries have also been imaged in HREM. Tetragonal precipitate colonies which occur on annealing certain  $ZrO_2$ - $Y_2O_3$  alloys have also been studied. Each colony consists of alternating variants which are  $90^\circ$  twins. HREM shows that the twin boundaries are highly coherent with a slight tilt between the variants. The "matrix" between the tetragonal colonies is shown by optical diffraction analysis of the HREM images to have tetragonal rather than cubic symmetry, indicating the occurrence of a diffusionless cubic  $\rightarrow$  tetragonal transformation.

### 1. Introduction

$ZrO_2$ -containing ceramics have attracted much attention in recent years because of their unusual mechanical and electrolytic properties [1,2]. Their considerable potential for high-technology structural applications derives from the phenomenon of *transformation toughening*. Briefly,  $ZrO_2$  is polymorphic, the three polymorphs being shown in fig. 1 [3]. The high-temperature form is cubic and is isostructural with  $CaF_2$  (fluorite structure). At temperatures below  $\sim 2350^\circ C$  for pure  $ZrO_2$ , or at temperatures considerably lower for  $ZrO_2$  alloys, the cubic polymorph (*c*- $ZrO_2$ ) transforms to a tetragonally distorted version of the fluorite structure, shown in fig. 1b (*t*- $ZrO_2$ ). At still lower temperatures, *t*- $ZrO_2$  transforms martensitically to the monoclinic structure shown in fig. 1c (*m*- $ZrO_2$ ). This martensitic *t*  $\rightarrow$  *m* transformation is the origin of transformation toughening in  $ZrO_2$ -containing ceramics, as will now be described.

In suitably fabricated ceramics, particularly if the *t*- $ZrO_2$  is present as fine particles, the start or *M<sub>s</sub>* temperature of the martensitic transformation,

which is  $\leq 1000^\circ C$  in pure bulk  $ZrO_2$ , can be reduced to below room temperature, i.e., the *t*- $ZrO_2$  is retained metastably at room temperature. However, the *t*  $\rightarrow$  *m* transformation can be induced by external stresses, for example, the stress field associated with a propagating crack. This stress-induced tetragonal-to-monoclinic transformation thus "shields" the crack tip from the applied stresses and is the origin of the improved strength and toughness of transformation-toughened  $ZrO_2$ -containing ceramics.

It should be clear from this introduction that the type, amount, morphology and distribution of the  $ZrO_2$  polymorphs within  $ZrO_2$ -containing ceramics are of prime importance, and both homophase ( $ZrO_2/ZrO_2$ ) and heterophase ( $ZrO_2$  particle/non- $ZrO_2$  matrix) interfaces are of interest. In fact, such studies of interfaces in polycrystalline, polyphase ceramics are crucial for understanding the variety of diffusional and diffusionless transformations that are important when considering microstructural evolution during fabrication and performance during service. Inasmuch as HREM can play a vital role in understanding

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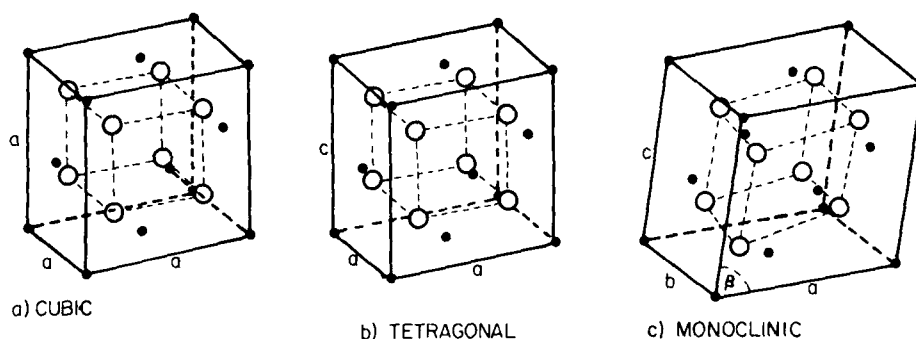


Fig. 1. Three polymorphs of  $\text{ZrO}_2$ : (a) cubic phase; (b) tetragonal phase,  $c/a \approx 1.02$ ; (c) monoclinic phase. The small filled spheres are Zr atoms, the large open spheres are oxygen.

these technologically important ceramics, we have begun a broad program using high-resolution electron microscopy to study interfaces in such ceramics.

## 2. Experimental procedures

15 vol%  $\text{ZrO}_2$ -toughened  $\text{Al}_2\text{O}_3$  (ZTA) specimens were obtained from Dr. N. Claussen (Max-Planck-Institut für Metallforschung, Stuttgart, Fed. Rep. of Germany). The starting powders were Alcoa A-16  $\text{Al}_2\text{O}_3$  and Magnesium Electron ARZ52  $\text{ZrO}_2$ . Processing consisted of attritor milling for 12 h, followed by hot pressing at  $1550^\circ\text{C}$  for 30 min; the density of the resulting ceramic was 99.5% of theoretical.

Single crystal skull-melted  $\text{ZrO}_2$ -8 wt%  $\text{Y}_2\text{O}_3$  was obtained from the Ceres Corporation. This material was then heat-treated for 50 h at  $1600^\circ\text{C}$  and furnace-cooled; Laue back-reflection photographs were used to orient the crystal to a  $\langle 111 \rangle$  zone.

Both materials were prepared for TEM examination using standard techniques, i.e. diamond-wafering thin slices, grinding and polishing to approximately  $50\ \mu\text{m}$  thickness, followed by ion-beam thinning to electron transparency. A thin carbon coat was sputtered on one surface before insertion into a JEOL 200CX having a  $C_s$  of 1.1 mm and a point resolution of  $\leq 0.24\ \text{nm}$ . An Intellect 200 image analysis system is used for

on-line image processing; Skarnulis' CELLS program [4] is available for image simulation.

## 3. Zirconia-toughened alumina

ZTA, an example of a wider class of dispersion-toughened ceramics, is one of the three useful types of  $\text{ZrO}_2$ -containing ceramics. These materials typically contain 15 vol%  $\text{ZrO}_2$  in a fine-grained  $\text{Al}_2\text{O}_3$  matrix; the  $\text{ZrO}_2$  can be *inter-* or *intragranular* and the propensity for undergoing the martensitic transformation depends markedly on the morphology of the  $\text{ZrO}_2$  particles [5]. Furthermore, the stability of *t*- $\text{ZrO}_2$ , i.e. its resistance to undergoing the martensitic transformation, involves stress concentrations at interfaces. It now appears that nucleation of the *t*  $\rightarrow$  *m* martensitic transformation is always stress-assisted [6], and the magnitude of these stresses is very sensitive to particle morphology [7]. Understanding of the *t*  $\rightarrow$  *m* martensitic transformation depends on increased knowledge of the interface structure, and a variety of  $\text{ZrO}_2$ - $\text{Al}_2\text{O}_3$  interfaces have been imaged with high-resolution electron microscopy.

The first example is shown in fig. 2. A roughly spherical *m*- $\text{ZrO}_2$  particle is completely enclosed within an  $\text{Al}_2\text{O}_3$  grain. As has been discussed elsewhere [8], this morphology arises from "break-away" grain growth of  $\text{Al}_2\text{O}_3$  grain boundaries during densification or extended high-temperature

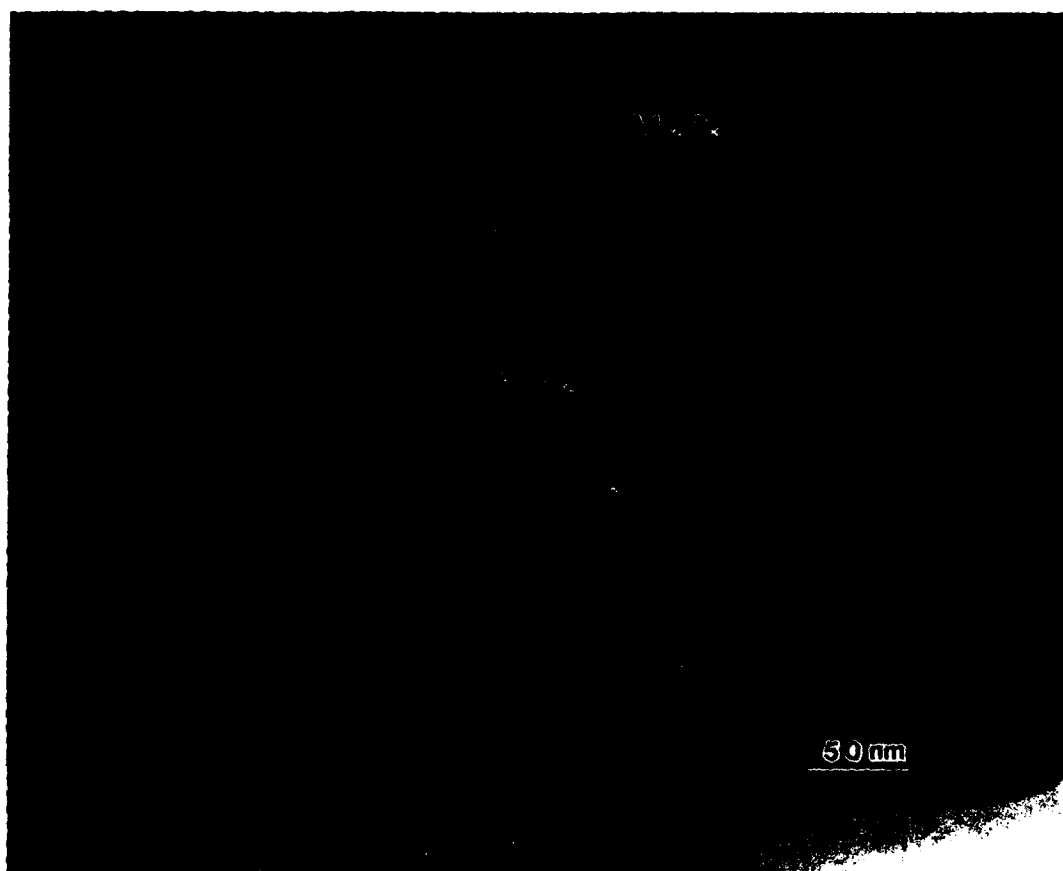


Fig. 2. Bright-field micrograph of intragranular  $\text{ZrO}_2$  particle in  $\text{Al}_2\text{O}_3$  grain.

annealing. While particles such as these are generally resistant to the martensitic transformation in bulk ceramics [5], foil preparation has been found to induce the  $t \rightarrow m$  transformation, especially if, as in the present case, the  $\text{ZrO}_2$  is free of any "stabilizer" solute. Thus, the  $\text{ZrO}_2$  particle shown in fig. 2 has  $m$  symmetry, having transformed during foil preparation, and a conventional selected-area diffraction pattern of both the  $\text{ZrO}_2$  particle and the  $\text{Al}_2\text{O}_3$  matrix (not shown here) reveals the fortunate circumstance that the particle and matrix are oriented such that both are within a few degrees of a low-index zone axis orientation, [001] for  $\text{ZrO}_2$  and [0001] for  $\text{Al}_2\text{O}_3$ . Furthermore, the foil is of relatively uniform thickness over the

whole area of fig. 2, and could be imaged in HREM. A structure image of the  $\text{ZrO}_2$  particle after tilting to the exact [001] orientation is shown in fig. 3, along with an image calculated by computer simulation. It is clear that the image matching in this particular instance is acceptable. We also hope to model the interfaces (at regions 1–4 in fig. 2 to be shown next), although such interface simulations have not yet been completed.

The particle–matrix interface is shown at higher resolution in fig. 4: the  $\text{ZrO}_2$  is oriented exactly on the zone axis in fig. 4a, while the  $\text{Al}_2\text{O}_3$  is oriented exactly on the zone axis in fig. 4b. The feature marked F in figs. 4a and 4b is a fault in the  $m$ - $\text{ZrO}_2$  which we have not yet analyzed. The

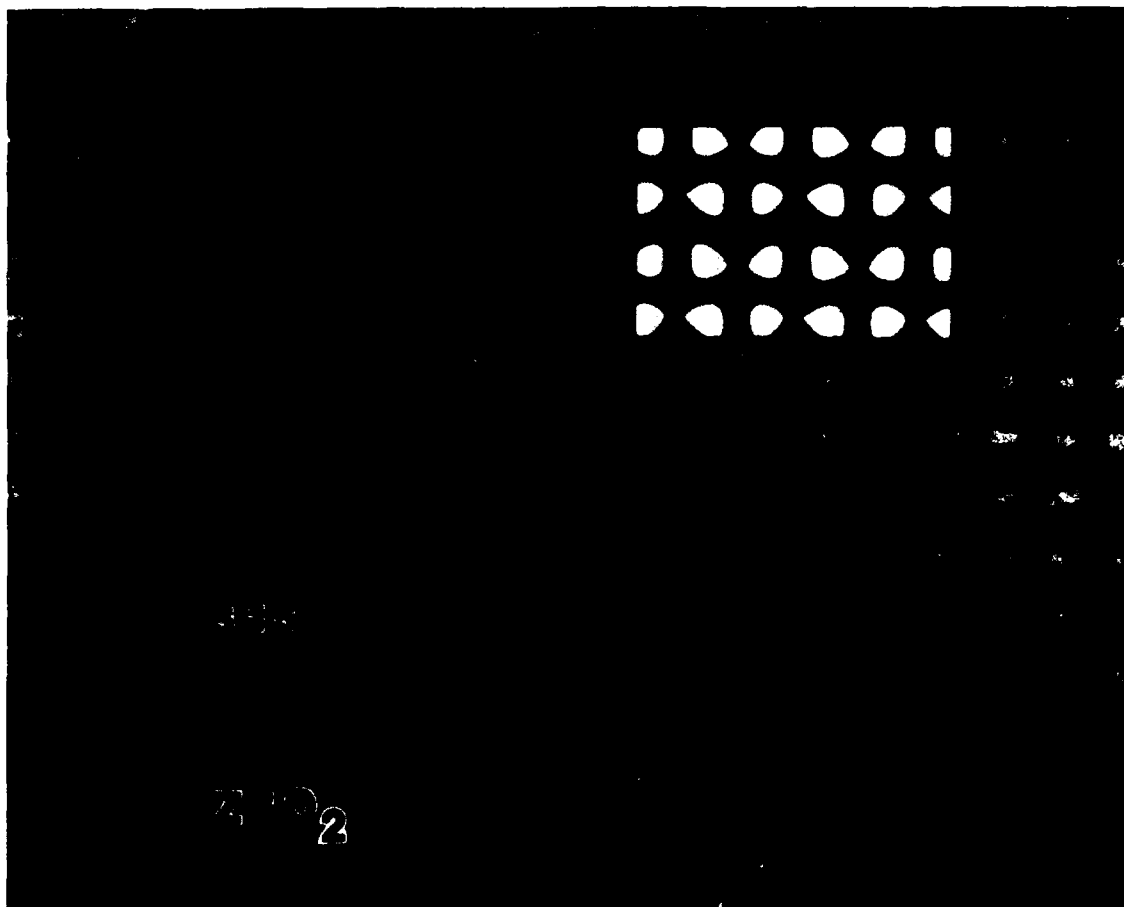


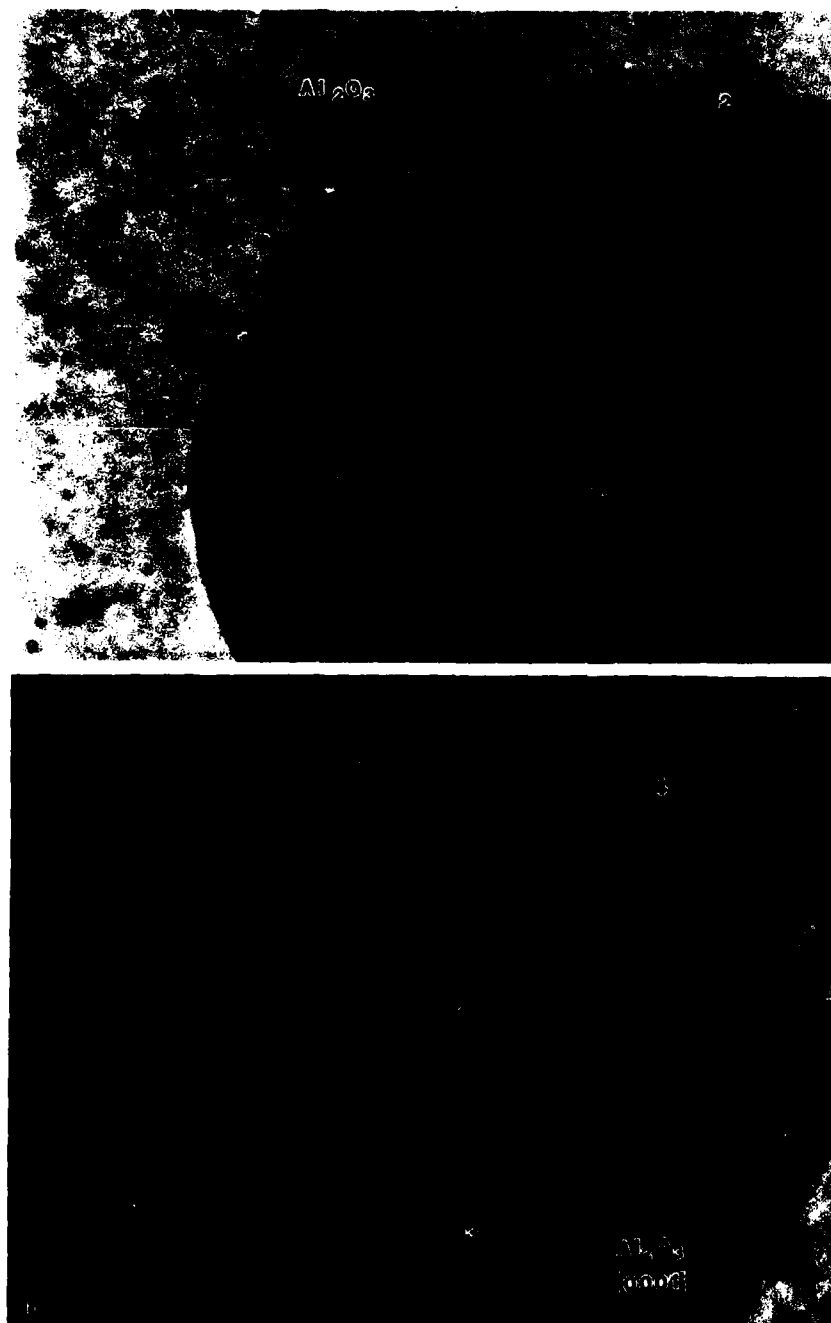
Fig. 3. High-resolution image of  $[001]_m \text{ZrO}_2$ , with calculated image match. The unit cell is shown.

features marked 1 and 2 in fig. 4a denote particular interface regions which are shown at higher magnifications in fig. 5. We believe that the interface is most nearly parallel to the electron beam in region 1 in fig. 5a, and expect that sensible image interpretation of the atomic structure of this interface will be possible. On the other hand, the region shown in fig. 5b is judged to be uninterpretable because the interface is inclined to the electron beam; no further analysis is being contemplated for this image.

Slight tilting brings the  $\text{Al}_2\text{O}_3$  grain into its symmetry position, and fig. 6 shows two regions (marked 3 and 4) on the opposite side of the

faulted particle. Fig. 6a shows an area in which the interface is more or less parallel to the electron beam and for which we hope to provide suitable image simulations in the near future. Fig. 6b, on the other hand, shows a region of interface that is inclined to the electron beam and is judged unsuitable for further interpretation. Figs. 5a and 6a are remarkable in that they show the images extend right to the  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  interface, and that this *incoherent* interphase interface appears to accommodate the two dissimilar lattices without undue difficulty.

With regard to transformation toughening, intergranular particles are preferred in  $\text{ZrO}_2$ -



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Fig. 4. (a) Higher-magnification micrograph of  $\text{ZrO}_2$  particle in fig. 2 with interfacial regions 1 and 2 indicated. F is a fault in the particle. The foil is oriented so that  $\text{ZrO}_2$  is exactly on the  $[001]$  orientation. (b)  $\text{ZrO}_2$  particle with interfacial regions 3 and 4 indicated. The foil is oriented so that  $\text{Al}_2\text{O}_3$  is exactly on the  $[0001]$  orientation.



Fig. 5. (a) High-resolution image of interfacial region 1. (b) High-resolution image of interfacial region 2.

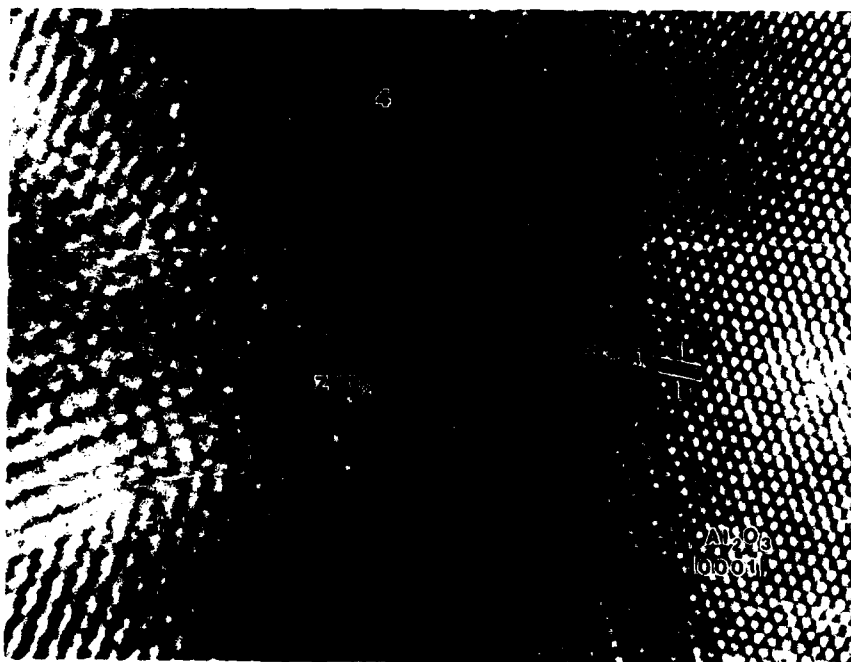


Fig. 6. (a) High-resolution image of interfacial region 3. (b) High-resolution image of interfacial region 4.

toughened  $\text{Al}_2\text{O}_3$ , and the sample of figs. 2–6 in fact contains more inter- than intragranular particles. However, it should be mentioned that virtually all  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$  grain boundaries and  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  intergranular boundaries in this sample are coated with a thin film (1–3 nm) of a  $\text{SiO}_2$ -containing amorphous phase (the  $\text{SiO}_2$  impurity having been introduced during processing); such a grain boundary phase appears to be ubiquitous in all the  $\text{ZrO}_2$ -toughened  $\text{Al}_2\text{O}_3$ 's studied to date. This glassy phase can best be imaged by forming a dark field image using diffuse inelastically scattered electrons. The glass is thus located at the bright regions in fig. 7 and the particular arrowed feature is glass along an  $\text{Al}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$  grain boundary. The presence of

such an amorphous phase at the  $\text{Al}_2\text{O}_3$ – $\text{ZrO}_2$  interface does not detract from detailed HREM studies of the interfaces. A HREM image of a twinned  $m$ - $\text{ZrO}_2$  particle in this sample is shown in fig. 8. (This is not the same region as shown in fig. 7.) The  $\text{ZrO}_2$  particle is extensively twinned, the twinning occurring during spontaneous transformation on cooling following fabrication. This twinning occurs to minimize the shape strain of the particle during the martensitic transformation, and is present in virtually all  $m$ - $\text{ZrO}_2$  particles, except those which have transformed in a thin foil, as in fig. 2.

The orientations of the two  $\text{Al}_2\text{O}_3$  grains and the several twinned “domains” of the  $\text{ZrO}_2$  particle were determined by taking optical diffracto-



Fig. 7. Diffuse dark-field micrograph of intergranular  $\text{ZrO}_2$  in an  $\text{Al}_2\text{O}_3$  matrix, showing glassy phase at grain boundaries. (The arrowed region is an  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$  boundary.)



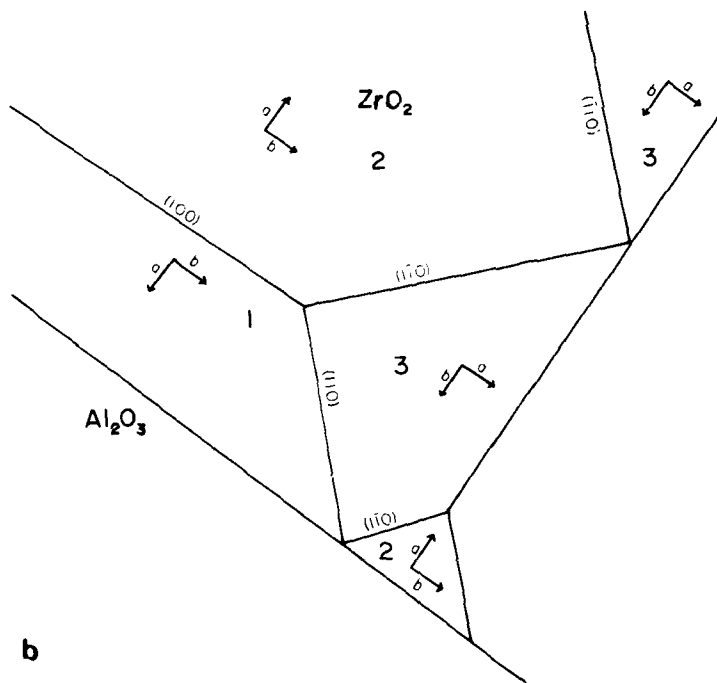
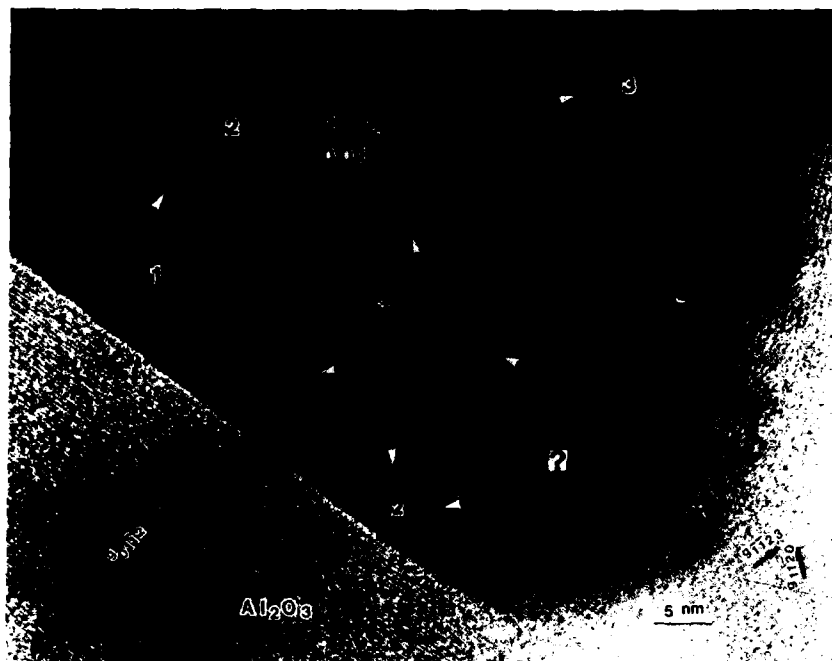


Fig. 8. (a) High-resolution image of intergranular  $\text{ZrO}_2$  particle showing microtwins. The twin boundaries are arrowed, as is an  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$  grain boundary. 1, 2, and 3 refer to specific twin orientations shown in (b); the question-mark is a region of serious overlap between the  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$ . (b) Diagram of (a) showing twin planes and orientations.

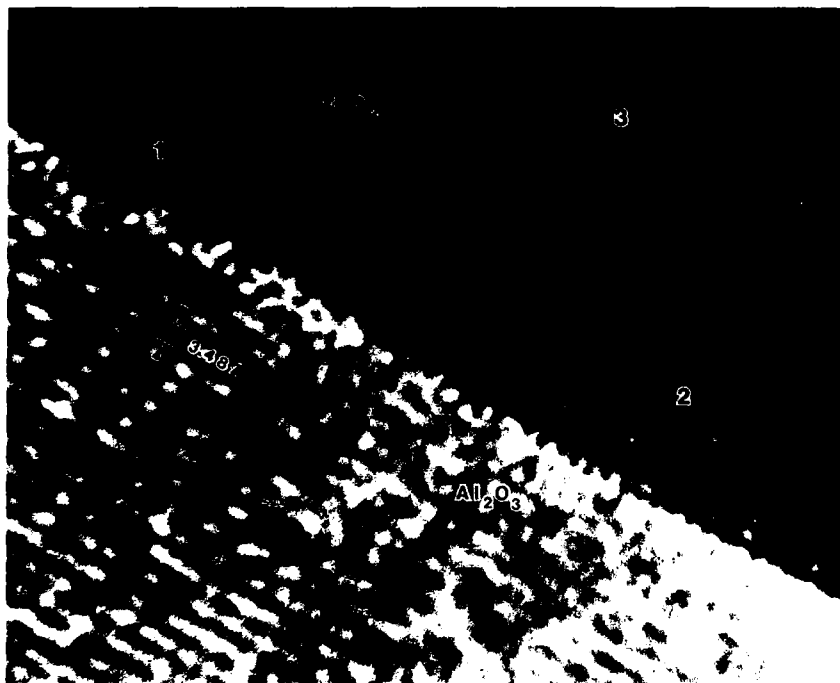


Fig. 9. High-resolution image of  $\text{ZrO}_2$  particle in fig. 8a showing possible glassy phase at grain boundary. 1, 2, and 3 refer to the twin orientations shown in fig. 8b.

grams from fig. 8a, and yielded the results shown schematically in fig. 8b. The morphology of the twinned domains, as well as the existence of  $(100)_m$ ,  $(110)_m$ , and  $(\bar{1}\bar{1}0)_m$  twin boundaries, are identical to the results described by Van Tendeloo et al. in  $\text{ZrO}_2$ -ZrN alloys [9].

The final figure for this section (fig. 9) shows the  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  interface at high magnification. It is tempting to argue that the broad bright region between the  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  is a manifestation of the amorphous phase believed to be present, but image simulation is clearly needed to resolve this point. Even lacking such image simulation, it is again remarkable that the features in the structure image extend virtually undisturbed to the incoherent interphase interface. (It is fortunate that the interface in this region of foil is essentially parallel to the electron beam.)

#### 4. $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$ alloys

$\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$  alloys represent a second major class of  $\text{ZrO}_2$ -containing ceramics which have also been subject to significant commercial exploitation. Low  $\text{Y}_2\text{O}_3$ -content (2-4 mol%) compositions in this system are in use as strong and tough wear-resistant ceramics [10]; medium  $\text{Y}_2\text{O}_3$ -content (4-8 mol%) compositions find use as oxygen sensors in automotive application [11]; and single crystals containing ~10 mol%  $\text{Y}_2\text{O}_3$  are used as imitation diamonds [12]. We have been studying phase equilibria at temperatures between 1300 and 1600°C in this system using a range of compositions between 3 and 9 mol%  $\text{Y}_2\text{O}_3$ . Our strategy is to anneal various compositions for long times to allow the pro-eutectoid precipitation reaction to go to completion and to use analytical electron mi-

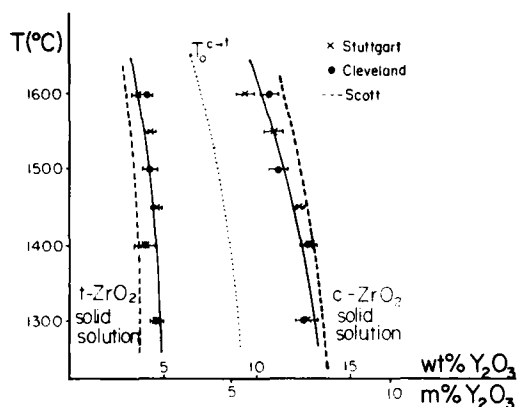
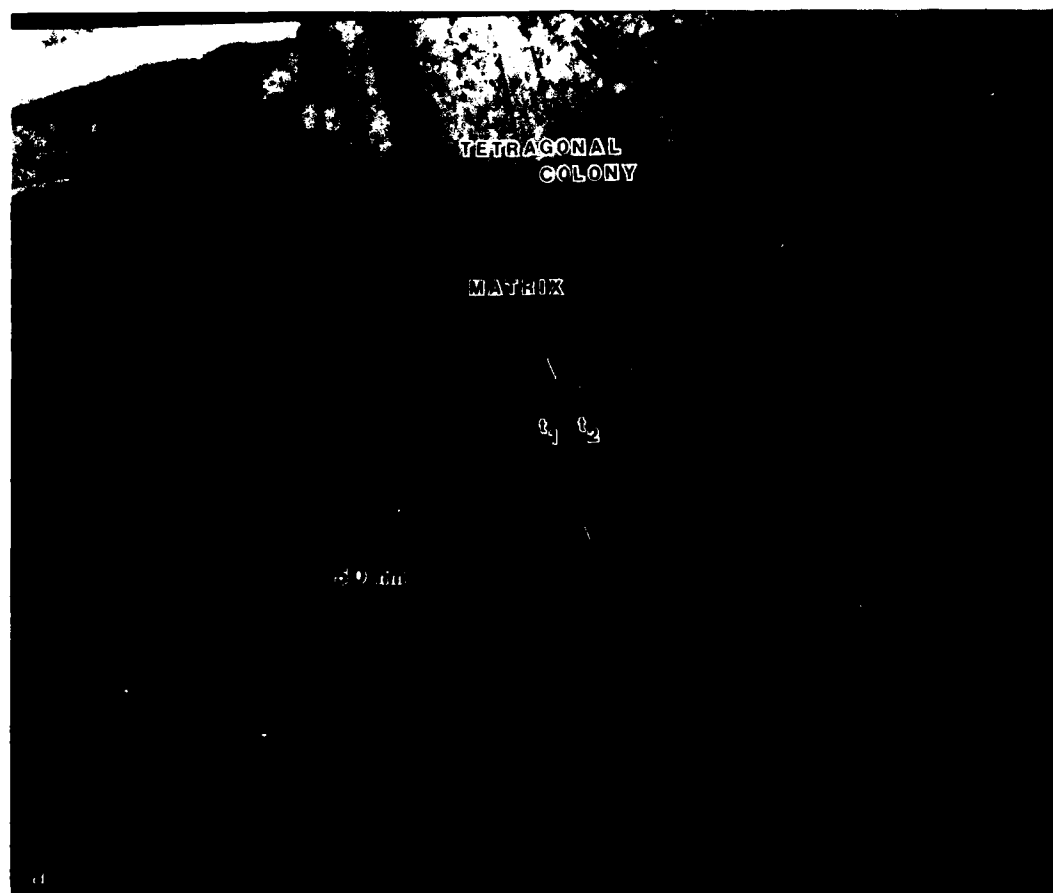


Fig. 10.  $\text{ZrO}_2$ -rich portion of the equilibrium phase diagram in the  $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$  system. The equilibrium compositions were determined by EDS methods.

croscopy to study the compositions of the coexisting  $c$  and  $t$  solid solutions ( $\text{Y}_2\text{O}_3$  is very potent in stabilizing  $t\text{-ZrO}_2$  and reducing  $M_1$  well below room temperature) [3]. The results of these AEM studies are shown in the partial phase diagram in fig. 10 [3]. For most compositions in the two-phase  $t + c$  solid solution phase field, the  $t\text{-ZrO}_2$  occurs as twinned "colonies", whose structure will be discussed in the remainder of this paper. The colony structure is shown in fig. 11a; this micrograph is taken from a 4 mol%  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  single crystal oriented to an exact  $\langle 111 \rangle$  matrix zone-axis orientation. Each colony contains two  $t$  variants, which are actually  $90^{\circ}$  twins (fig. 11b); this morphology occurs to minimize strain between the colony precipitates and the matrix. As will be discussed next, the matrix also has tetragonal sym-



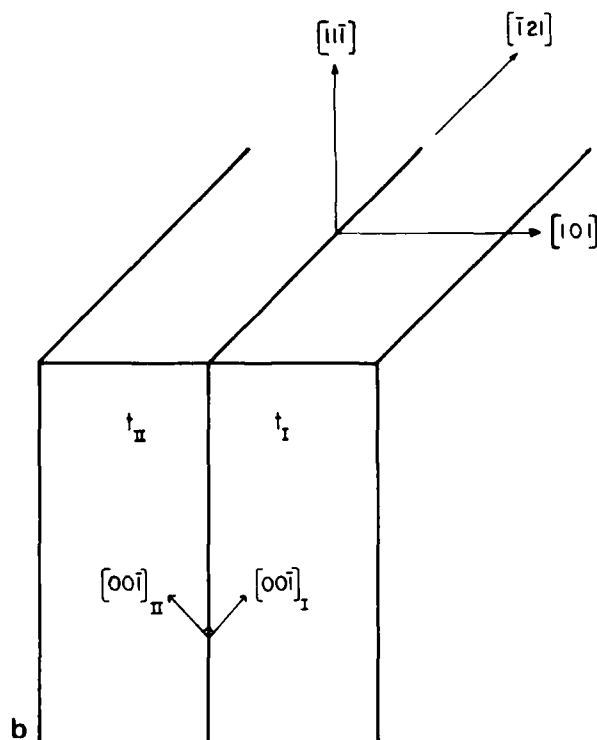


Fig. 11. (a) Tetragonal colony structure in  $\text{ZrO}_2$ -4 mol%  $\text{Y}_2\text{O}_3$  showing a typical interface of interest (arrowed). (b) Schematic diagram showing twin variant crystallography. (The interface is perpendicular to  $[101]$ .)

metry, having undergone a diffusionless  $c \rightarrow t$  transformation on cooling from the annealing temperature [3]. The twinned colony structure of the  $t$ - $\text{ZrO}_2$  precipitates is very stable even during extended annealing; the number of twins per colony remains constant even as the colonies coarsen [13].

A HREM image of a twin variant interface is shown in fig. 12; this interface is similar to the one arrowed in fig. 11a, but of course was taken in a thinner region of the foil. It can be seen that the  $(1\bar{1}0)$  planes are imaged in one  $t$  variant, while the  $(2\bar{2}0)$  planes are imaged in its twin. This difference is believed to result from the very small tilt of one twin relative to the other, and would not occur were the  $c/a$  ratio exactly unity.

The origin of the colony stability is also apparent from fig. 12. The twin interface of fig. 12 (marked TB) can hardly be discerned; were it not for the slight tilt of the two twins, the twin

boundary might not be visible. The good atomic matching thus implied assures that the twin boundary energy is correspondingly low. Thus, interface energy in the twinned structure must always be less than the reduced strain energy between colony precipitate and matrix.

The HREM study has also helped resolve a question concerning the matrix crystallography. As first suggested by Scott [14], and as is discussed elsewhere [3,13,15],  $c$ - $\text{ZrO}_2$  alloys quenched from high temperature can undergo a displacive  $c \rightarrow t$  transformation below a certain critical temperature,  $T_0$ . (The variation in  $T_0$  with composition is indicated by the dashed line in fig. 10 marked  $T_0' \rightarrow t$ .) The equilibrium composition of the  $c$ - $\text{ZrO}_2$  matrix annealed at  $1600^\circ\text{C}$  is 6.0 mol%  $\text{Y}_2\text{O}_3$ ;  $T_0$  for this composition is  $\sim 900^\circ\text{C}$ . We thus expect both the matrix and the colonies of fig. 11 to have  $t$  symmetry, but to differ in  $\text{Y}_2\text{O}_3$  content by a

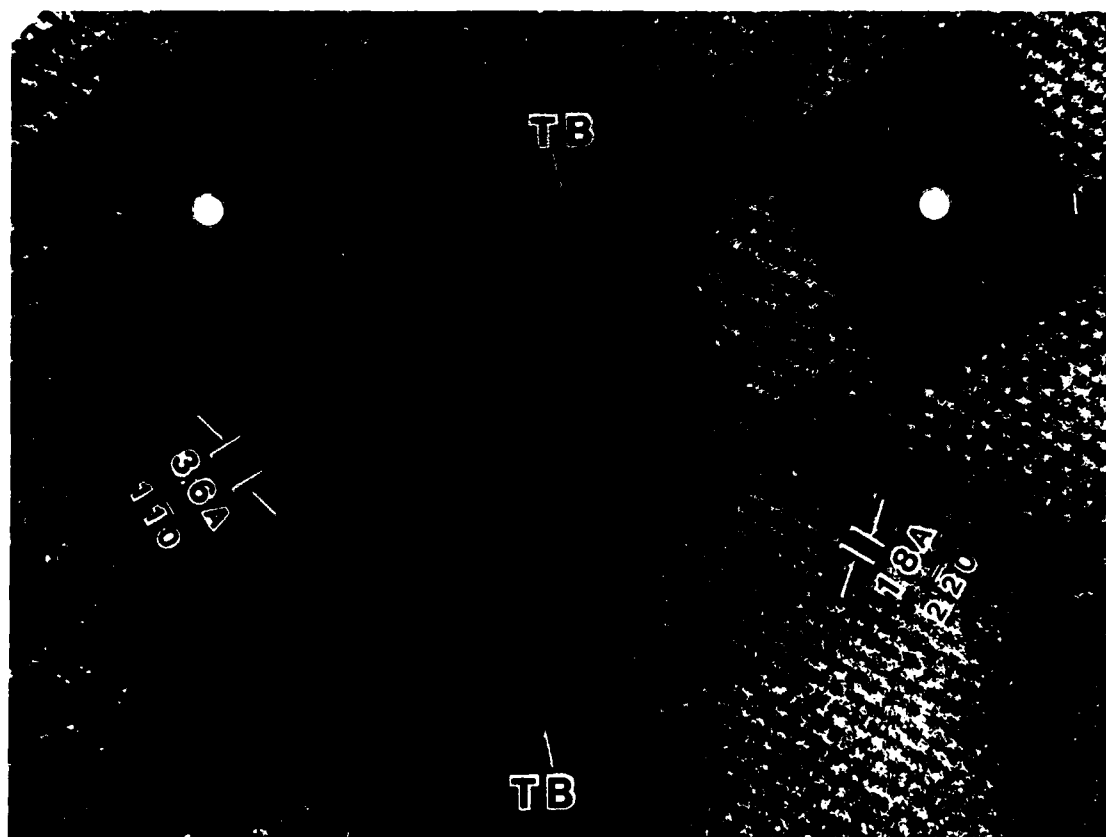


Fig. 12. High-resolution image of a coherent twin boundary (TB) between two tetragonal variants within the same colony. Optical diffractograms are shown as inserts.

factor of  $\sim 3$ . This chemical difference has been confirmed by AEM [13]. However, the variation in lattice parameter with  $Y_2O_3$  solute is too small in this system to give rise to any spot splitting in the *odd, odd, even* reflections unique to *t*- $ZrO_2$  in conventional large-area SAD patterns, and it is difficult to be certain that there is no contribution from the colonies in any SAD pattern taken only from the matrix.

Fig. 13 shows a high-resolution image of the matrix, along with two optical diffractograms taken from different regions of the image. The  $\{220\}$

planes with 0.18 nm spacing imaged on the left portion of fig. 13 are consistent with either *c* or *t* symmetry. Slight bending of the foil has caused the adjacent area to be slightly off the exact orientation. In this region, (110) planes with 0.36 nm spacing are being imaged. (110) is a forbidden reflection for both *c*- $ZrO_2$  and *t*- $ZrO_2$ , but often occurs in *t*- $ZrO_2$  by double diffraction from (112) planes. In any event, this spacing in the optical diffraction pattern is unambiguous evidence that the matrix has undergone the *c*  $\rightarrow$  *t* transformation.

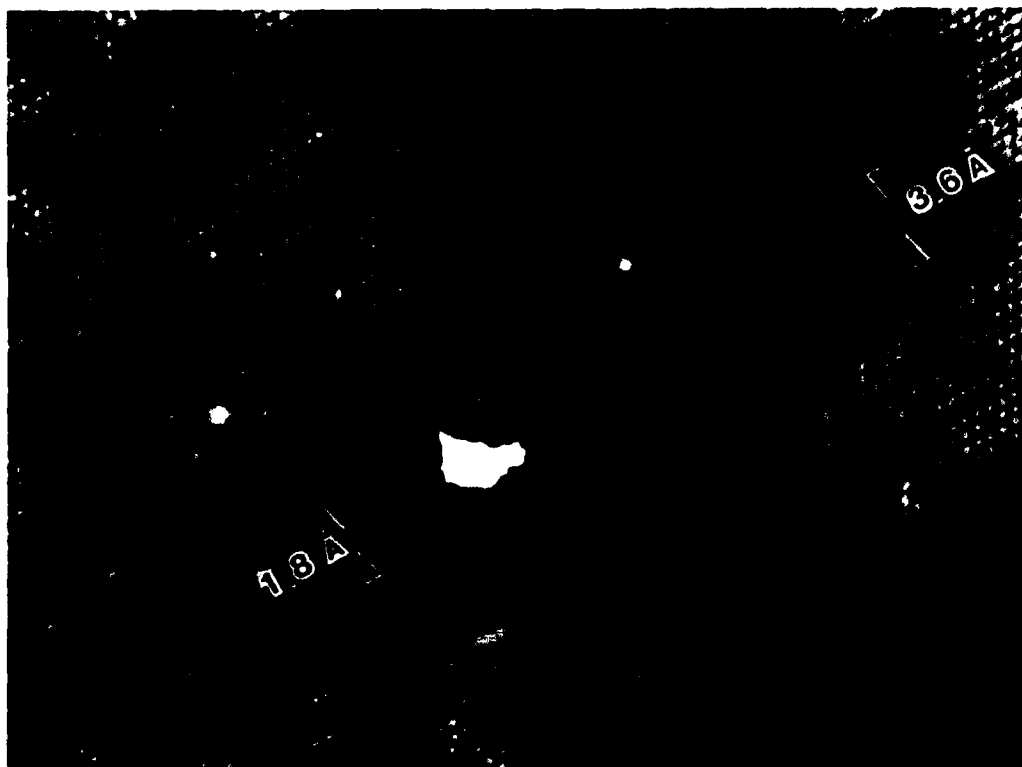


Fig. 13. High-resolution image and optical diffractograms of the matrix between two colonies.

### Acknowledgments

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